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Reactivity of $Ph_2(2\text{-}C_5H_4N)PSe$ towards $Ru_3(CO)_{12}$ and mononuclear $MCl_2(PhCN)_2$ (M = Pd or Pt) complexes

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Dedicated to the dear friend Pierre Braunstein in recognition of his brilliant career and of his important contributions to the development of inorganic chemistry.

Abstract

The behavior of the $Ph_2(2\text{-}C_5H_4N)PSe$ ligand in the reactions with $Ru_3(CO)_{12}$ and the mononuclear complexes $MCl_2(PhCN)_2$ (M = Pd or Pt) has been investigated. The reaction with $Ru_3(CO)_{12}$ is characterized by P=Se bond cleavage, affording the 48-electron compound $[Ru_3(\mu_3\text{-Se})(\mu\text{-PPh}_2)_2(\mu\text{-}C_5H_4N)(\mu_3\text{-}C_5H_4N)(CO)_6]$ (**1**), the open triangular 50-electron *nido* clusters $[Ru_3(\mu_3\text{-Se})_2(CO)_{9-n}\{P(2\text{-}C_5H_4N)Ph_2\}_n]$ (**2** and **3**, for $n = 1$ and 2, respectively) and the octahedral 62-electron *closo* cluster $[Ru_4(\mu_4\text{-Se})_2(CO)\{\mu\text{-}P,N\text{-}Ph_2(2\text{-}C_5H_4N)P\}]$ (**4**). The cluster **1** derives by the multiple fragmentation of two phosphine ligands on the metal triangle involving the P=Se and P–C bond cleavages. The molecular structure of **4** shows a short Ru···P non-bonding separation that can be viewed as a preliminary step towards the P–C bond cleavage. In the reactions with $MCl_2(PhCN)_2$ (M = Pd, Pt) $Ph_2(2\text{-}C_5H_4N)PSe$ remains intact affording mononuclear neutral complexes of the type $MCl_2\{N,Se\text{-}Ph_2(2\text{-}C_5H_4N)PSe\}$. The crystal structure of the palladium derivative **5** has been determined by X-ray diffraction methods.

Keywords: Ruthenium; Palladium; Platinum; Selenido-bridged complexes; Pyridyl-bridged complexes; Cluster compounds; Crystal structures

1. Introduction

Transition metal species may combine with main group elements or related molecular fragments affording a variety of interesting cluster compounds. Apart from their fundamental significance as a class of complexes owning peculiar chemical and structural properties, the growing interest for these species derives from their potential application both as catalysts and as precursors for semiconductors with low band-gaps [1].

In recent years we have carried out systematic investigations on the selenium transfer reactions by tertiary phosphine and diphosphine selenides, such as Ph_3PSe, $CH_2(Ph_2PSe)_2$, $CH_2CH_2(Ph_2PSe)_2$, and $Fe(\eta^5\text{-}C_5H_4P(Ph_2)Se)_2$, towards iron and ruthenium carbonyl clusters [2]. These reactions, taking advantage from the frailty of the P=Se bond, provide a simple, one-step, synthetic route to phosphine-substituted, mono- and diselenido trinuclear clusters. In some cases these reactions are very selective: the stoichiometric control combined with different experimental conditions allowed us to obtain the disubstituted trinuclear cluster $Ru_3(\mu_3\text{-Se})_2(CO)_7(PPh_3)_2$ in very high yield (> 90%) [3]. On the other hand, they can lead to the formation of different species not easily achievable by other routes, such as the cubane-like cage complex $[Ru_4(\mu_3\text{-Se})_4(CO)_{10}\{\mu\text{-}P,P\text{-}(Ph_2P)_2CH_2\}]$ [4].

As a natural extension of these investigations, we have studied the reactions of Group-8 carbonyl clusters with tertiary phosphine selenides bearing heterocyclic groups, namely $2\text{-}C_5H_4N$(2-pyridyl), $2\text{-}C_4H_3S$(2-thienyl) and 5-(2-pyridyl)-2-thienyl. The presence of these groups was

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expected to lead to new reactivity patterns in cluster growing processes, owing to the coordinating ability of the hetero-atoms and to the possible release of heterocyclic fragments. Actually, in these reactions the expected transfer of the chalcogenido atom to the metal cluster can be followed by P–C bond cleavage, affording new selenido–phosphido clusters. In particular, in the case of thienyl and thienylpyridyl groups, the 48-electron clusters $[Ru_3(\mu_3\text{-}Se)(\mu\text{-}PPh_2)(\mu\text{-}R)(CO)_6\{P(R)Ph_2\}]$ [R = 2-thienyl or 5-(2-pyridyl)-2-thienyl] were obtained in good yields by a one-step synthesis [5,6]. Their molecular structures show the concomitant presence of the diphenylphosphido (bridging one side) and selenido (capping) ligands on the same cluster core.

Regarding the pyridyl ring, the ligands $Ph_2(2\text{-}C_5H_4N)P$ and $Ph_2(2\text{-}C_5H_4N)PS$ have already been used in reactions towards transition metal complexes [7]. More recently we have synthesized the selenium derivative $Ph_2(2\text{-}C_5H_4N)PSe$ [8] and reacted it with monometallic and bimetallic transition metal clusters [8,9]. In the first case the reaction with $Ru_3(CO)_{12}$ affords the compound $[Ru_3(\mu_3\text{-}Se)(\mu\text{-}PPh_2)_2(\mu\text{-}C_5H_4N)(\mu_3\text{-}C_5H_4N)(CO)_6]$ deriving from multiple fragmentation of the phosphine. In the second case the bimetallic $[(CO)_3Fe(\mu_3\text{-}Se)\{Pt(CO)P(2\text{-}C_5H_4N)Ph_2\}_2]$ was obtained from the reaction with $[Fe_2(NO)_2(CO)_6\text{-}Pt(PhCN)_2]$.

The present paper, besides giving complete information about the reaction of $Ph_2(2\text{-}C_5H_4N)PSe$ with $Ru_3(CO)_{12}$, including the crystal structure of $[Ru_3(\mu_3\text{-}Se)_2(CO)_8\{P\text{-}Ph_2(2\text{-}C_5H_4N)P\}]$ and $[Ru_4(\mu_4\text{-}Se)_2(CO)_9\text{-}\{\mu\text{-}P,N\text{-}Ph_2(2\text{-}C_5H_4N)P\}]$, deals with the formation of mononuclear Pt and Pd complexes of the type $MCl_2\{N,Se\text{-}Ph_2(2\text{-}C_5H_4N)PSe\}$ in which the P=Se bond cleavage is not observed.

2. Experimental

2.1. General remarks

The starting reagents $[Ru_3(CO)_{12}]$, KNCSe, $Ph_2(2\text{-}C_5H_4N)P$, Me_3NO, $MCl_2(PhCN)_2$ (M = Pd or Pt) were pure commercial products (Aldrich and Fluka) and were used as received. $Ph_2(2\text{-}C_5H_4N)PSe$ was synthesized according to the literature procedure [8]. The solvents (Carlo Erba) were dried and distilled by standard techniques before use. All manipulations (prior to the TLC separations) were carried out under dry nitrogen by means of standard Schlenk-tube techniques. Elemental (C, H, N) analyses were performed with a Carlo Erba EA 1108 automated analyzer. IR spectra (KBr discs or CH_2Cl_2 solutions) were recorded on a Nicolet 5PC FT spectrometer. ^1H (300 MHz), ^{31}P (81.0 MHz, 85% H_3PO_4 as external reference) NMR spectra ($CDCl_3$ solutions) were recorded on Bruker instruments, AC 300 (^1H) and CXP 200 (^{31}P).

2.2. Reactions of $Ph_2(2\text{-}C_5H_4N)PSe$ with $[Ru_3(CO)_{12}]$

The experimental details are described in a previous paper [8] along with the spectroscopical characterization of **1** (main experimental details are given in Scheme 1). Purification by crystallization (from a CH_2Cl_2–MeOH mixture at 5 °C for some days) gave well formed crystals of **3** and **4** suitable for X-ray analysis.

2.3. Cluster **2**

FT IR (CH_2Cl_2) $\nu(CO)$ (cm^{-1}): 2066, 2005, 1950. $^{31}P\{^1H\}$ NMR ($CDCl_3$, 25 °C): δ 20.9 (s).

2.4. Cluster **3**

FT IR (CH_2Cl_2) $\nu(CO)$ (cm^{-1}): 2047s, 2016, 1971, 1951sh. $^{31}P\{^1H\}$ NMR ($CDCl_3$, −30 °C): δ 53.5 (s), 42.7 (s). ^1H NMR ($CDCl_3$, 25 °C): δ 8.79 (d, 2H 2Py, ^3J(H,H) 4 Hz), 7.67–7.31 (m, 26H 4Ph, 2Py).

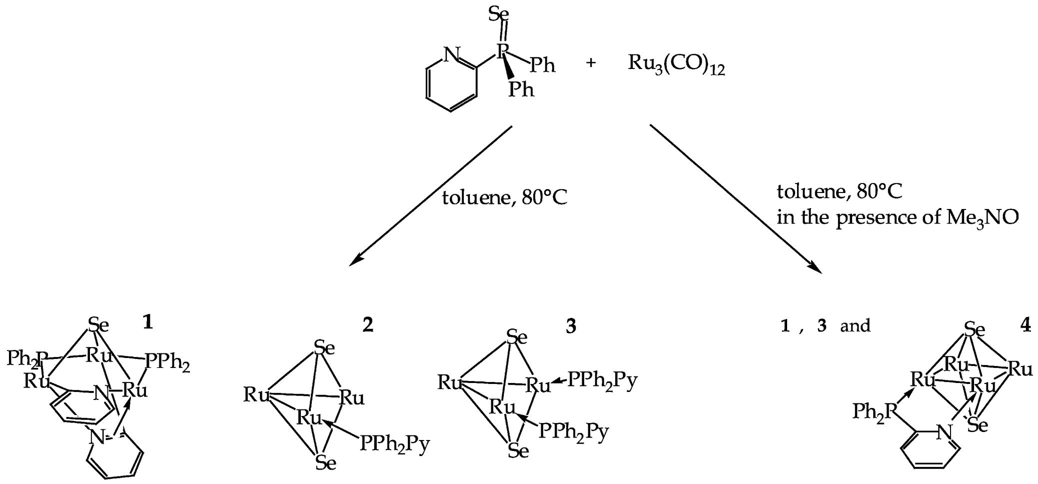
2.5. Cluster **4**

FT IR (CH_2Cl_2) $\nu(CO)$ (cm^{-1}): 2051s, 2020, 2005sh, 1972. $^{31}P\{^1H\}$ NMR ($CDCl_3$, 25 °C): δ 18.1 (s). ^1H NMR ($CDCl_3$, 25 °C): δ 9.25 (d, 1H Py, ^3J(H,H) 5.3 Hz), 7.79 (t, 1H Py, $^3J(H,P) = {}^3J(H,H)$ 7.8 Hz), 7.53–7.39 (m, 12H 2Ph, Py).

2.6. Reaction of $Ph_2(2\text{-}C_5H_4N)PSe$ with $PdCl_2(PhCN)_2$. Synthesis of $PdCl_2\{N,Se\text{-}Ph_2(2\text{-}C_5H_4N)PSe\}$ (**5**)

To a CH_2Cl_2 solution of $PdCl_2(PhCN)_2$ (0.130 g, 0.33 mmol) an equivalent quantity of $Ph_2(2\text{-}C_5H_4N)PSe$ (0.120 g, 0.33 mmol) dissolved in dichloromethane was added. The resulting orange solution was stirred for 1.5 h, then the solvent was removed in vacuo to obtain an orange–red powder. Purification by crystallization (from a CH_2Cl_2–MeOH mixture at 5 °C for some days) gave well-formed red crystals of **5** (yield 57%), suitable for X-ray analysis.

Compound **5**. *Anal*. Found: C, 39.5; H, 2.8; N, 2.7. Calc. for $C_{17}H_{14}Cl_2NPPdSe$: C, 39.4; H, 2.7; N, 2.7%. FT IR (KBr, cm^{-1}): 773m, 754m, 731m, 717m, 700m, 692m, 683m (fingerprints region) 551s (νPSe). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 34.2 (s, with ^{77}Se satellites, ^1J(P,Se) 280 Hz).



Scheme 1.

2.7. Reaction of $Ph_2(2\text{-}C_5H_4N)PSe$ with $PtCl_2(PhCN)_2$. Synthesis of $PtCl_2\{N,Se\text{-}Ph_2(2\text{-}C_5H_4N)PSe\}$ (**6**)

To a CH_2Cl_2 solution of $PtCl_2(PhCN)_2$ (0.207 g, 0.44 mmol) an equivalent quantity of $Ph_2(2\text{-}C_5H_4N)PSe$ (0.150 g, 0.44 mmol) dissolved in dichloromethane was added. The resulting yellow solution was stirred for 1.5 h, then the solvent was removed in vacuo to obtain an yellow powder.

Compound **6**. *Anal*. Found: C, 33.5; H, 2.2; N, 2.3. Calc. for $C_{17}H_{14}Cl_2NPPtSe$: C, 33.6; H, 2.3; N, 2.3%. FT IR (KBr, cm^{-1}): 771m, 754m, 731m, 718m, 701m, 691sh, 684m (fingerprints region), 552s (νPSe).

2.8. Crystal structure determination of compounds **3**·CH_2Cl_2, **4**·$0.5CHCl_3$ and **5**

The intensity data of **3**·CH_2Cl_2 and **4**·$0.5CHCl_3$ were collected at room temperature on a Philips PW 1100 and a Siemens AED single-crystal diffractometer using graphite monochromated Mo Kα radiation (**3**·CH_2Cl_2 and **4**·$0.5CHCl_3$) and graphite monochromated Cu Kα radiation (**5**). Crystallographic and experimental details for the structures are summarized in Table 1.

An empirical correction for absorption was made [maximum and minimum value for the transmission coefficient was 1.000 and 0.678, 1.000 0.753, 1.000 and 0.457, respectively, for, **3**·CH_2Cl_2, **4**·$0.5CHCl_3$ and **5**] [10]. The structures were solved by Patterson and Fourier methods and refined by full-matrix least-squares procedures (based on F_o^2) (SHELX-97) [11] first with isotropic and then with anisotropic thermal parameters in the last cycles of refinement for all the non-hydrogen atoms excepting for the C and Cl atoms of the solvent in **3**·CH_2Cl_2 and in **4**·$0.5CHCl_3$. The chloroform molecule was found with the carbon atom disordered in two positions with an occupancy factor of 0.25. The hydrogen atoms were introduced into the geometrically calculated positions and refined riding on the corresponding parent atoms. In the final cycles of refinement a weighting scheme $w = 1/[\sigma^2F_o^2 + (0.0820P)^2]$, (**3**·$CH_2Cl_2$), $w = 1/[\sigma^2F_o^2 + (0.0982P)^2]$, (**4**·$0.5CHCl_3$) and $w = 1/[\sigma^2F_o^2 + (0.1706P)^2]$, (**5**), where $P = (F_o^2 + 2F_c^2)/3$ was used.

3. Results and discussion

3.1. Reactions of $Ph_2(2\text{-}C_5H_4N)PSe$ with $[Ru_3(CO)_{12}]$

The reaction between $Ph_2(2\text{-}C_5H_4N)PSe$ and $[Ru_3(CO)_{12}]$ affords the products sketched in Scheme 1 (carbonyls omitted), whose distribution depends on the reaction conditions.

Cluster **2** and **3** [*nido* core, seven skeletal electron pairs (sep)] should be regarded as the primary products of the attack of two selenide molecules to the metal triangle, whereas cluster **4** (*closo*, 7 sep) should derive from the *nido* homologous through thermal condensation and ligand exchange processes. Clusters of these two families are generally the main products in the reactions of iron and ruthenium carbonyls with phosphine selenides [2]. In addition, the starting triruthenium triangle undergoes multiple attack by two P–C(Py) groups, resulting in the formation of the unprecedented compound $[Ru_3(\mu_3\text{-}Se)(\mu\text{-}PPh_2)_2(\mu\text{-}C_5H_4N)(\mu_3\text{-}C_5H_4N)(CO)_6]$ (**1**), whose structure has been previously reported [8]. This polynuclear species is characterized by the presence of a nearly planar array of eleven atoms formed by two roughly coplanar fused rings, i.e. the heptaatomic RuPRuPRuCN cycle and one pyridyl ring. This cluster has been obtained from $Ph_2(2\text{-}C_5H_4N)PSe$ through P=Se and P–C(Py) bond cleavages, the latter process contrasting with the reactivity of $Ph_2(2\text{-}$

Table 1
Crystal data and structure refinement for **3**·CH_2Cl_2, **4**·$0.5CHCl_3$, and **5**

	3·CH_2Cl_2	**4**·$0.5CHCl_3$	**5**
Formula	$Ru_3Se_2P_2N_2O_7C_{41}H_{28}\cdot CH_2Cl_2$	$Ru_4Se_2PNO_9C_{26}H_{14}\cdot 0.5CHCl_3$	$PdSePNCl_2C_{17}H_{14}$
Formula weight	1268.65	1137.24	519.52
Crystal system	monoclinic	monoclinic	triclinic
Space group	$P2_1/n$	$P2_1/c$	$P1$
a (Å)	11.041(4)	10.125(3)	8.337(3)
b (Å)	30.662(5)	17.191(4)	9.142(3)
c (Å)	14.495(4)	20.980(5)	12.414(5)
α (°)	90	90	98.71(2)
β (°)	111.31(2)	102.94(3)	103.99(3)
γ (°)	90	90	89.99(2)
V (Å^3)	4572(2)	3559.0(16)	2313(1)
Z	4	4	2
D_{calc} (g cm^{-3})	1.843	2.122	1.903
$F(000)$	2464	2148	504
Crystal size	0.15 × 0.12 × 0.15	0.11 × 0.11 × 0.12	0.18 × 0.22 × 0.25
μ (cm^{-1})	28.07	39.15	140.64
Reflections collected	13 797	8830	3417
Reflections unique	13 337 [$R_{int} = 0.0453$]	8615 [$R_{int} = 0.0338$]	3417 [$R_{int} = 0.000$]
Observed reflections	8513 [$I > 2\sigma(I)$]	4389 [$I > 2\sigma(I)$]	2269 [$I > 2\sigma(I)$]
Final R indices, [$I > 2\sigma(I)$]	$R_1 = 0.0436$, $wR_2 = 0.1205$	$R_1 = 0.0502$, $wR_2 = 0.1506$	$R_1 = 0.0767$, $wR_2 = 0.2052$
R indices (all data)	$R_1 = 0.0871$, $wR_2 = 0.1475$	$R_1 = 0.1111$, $wR_2 = 0.1704$	$R_1 = 0.0970$, $wR_2 = 0.2213$

$R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; $wR_2 = [\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]]^{1/2}$.

$C_5H_4N)P$ towards $[Ru_3(CO)_{12}]$, which undergoes P–C(Ph) rupture [12].

Clusters **2** and **3** possess the well known $Ru_3(\mu_3\text{-}Se)_2$ core and they can be described as a squared pyramid with two ruthenium and two selenium atoms alternating on the basal plane and the third ruthenium atom at the apex of the pyramid. In **2** only one phosphine replaces a carbonyl group, whereas in **3** two phosphine ligands coordinate two ruthenium atoms at the base of the pyramid, replacing two carbonyls. The structure of **3** has been fully elucidated by the X-ray analysis, while that of **2** has been recognized by comparison of its spectroscopic data with those of the analogous compound $[Ru_3(\mu_3\text{-}Se)_2(CO)_8(PPh_3)]$ [2].

In the crystals of **3**, $[Ru_3(\mu_3\text{-}Se)_2(CO)_7\{P\text{-}Ph_2(2\text{-}C_5H_4N)P\}_2]$ complexes and dichloromethane molecules of solvation are present. A view of the structure of **3** is shown in Fig. 1 together with the atomic labeling system.

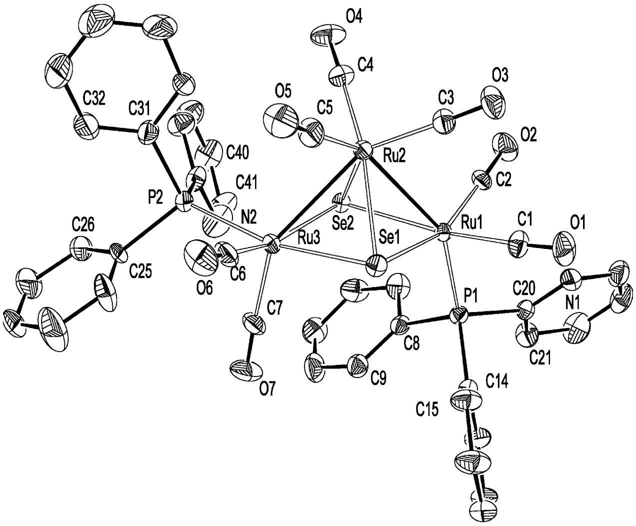


Fig. 1. View of the molecular structure of **3** together with the atomic numbering system. Thermal ellipsoids are drawn at 30% probability level.

Selected bond distances and angles are given in Table 2. The structure of **3** is very similar to that of the disubstituted analogue $Ru_3(\mu_3\text{-}Se)_2(CO)_7(PPh_3)_2$ [3]. In **3** the Ru-Se bonds range from 2.491(1) to 2.537(1) Å (2.491(1) to 2.536(2) Å in $Ru_3(\mu_3\text{-}Se)_2(CO)_7(PPh_3)_2$); the two Ru–Ru metal bond distances are comparable, 2.813(1) and 2.839(1) Å (2.801(2)–2.855(2) Å in $Ru_3(\mu_3\text{-}Se)_2(CO)_7(PPh_3)_2$), whereas the Ru–P ones, 2.306(1) and 2.354(2) Å (2.326(3)–2.371(4) Å in $Ru_3(\mu_3\text{-}Se)_2(CO)_7(PPh_3)_2$), differ remarkably because of the different *trans* influence of the Ru–Ru and Ru–Se bonds [3]. The structure of **3** is obviously also comparable to that of the unsubstituted analogue $Ru_3(\mu_3\text{-}Se)_2(CO)_9$ [13], where the values of the Ru–Ru bonds are 2.817(2) and 2.826(1) Å and those of the Ru–Se bonds are in the range 2.473(1)–2.526(1) Å. The ^{31}P NMR spectrum of cluster **3** recorded at 243 K exhibits two singlets, which collapse at 25 °C. This behavior indicates the non equivalence in solution of the two phosphorus atoms of the phosphine ligands, which occupy pseudo axial and pseudoequatorial non equivalent positions also in the solid state.

Table 2
List of selected bond lengths (Å) and angles (°) for **3**

Bond lengths	
Ru(1)–P(1)	2.3056(15)
Ru(1)–Se(2)	2.5027(8)
Ru(1)–Se(1)	2.5140(8)
Ru(1)–Ru(2)	2.8134(10)
Ru(2)–Se(1)	2.5299(8)
Ru(2)–Se(2)	2.5376(11)
Ru(2)–Ru(3)	2.8395(7)
Ru(3)–P(2)	2.3536(16)
Ru(3)–Se(2)	2.4915(8)
Ru(3)–Se(1)	2.5133(9)
P(1)–C(14)	1.822(6)
P(1)–C(8)	1.841(5)
P(1)–C(20)	1.854(5)
P(2)–C(37)	1.834(6)
P(2)–C(31)	1.841(6)
P(2)–C(25)	1.841(5)
Bond angles	
Se(2)–Ru(1)–Se(1)	79.89(3)
P(1)–Ru(1)–Ru(2)	151.49(4)
Se(1)–Ru(2)–Se(2)	78.93(2)
Ru(1)–Ru(2)–Ru(3)	85.32(2)
P(2)–Ru(3)–Se(1)	167.12(4)
Se(2)–Ru(3)–Se(1)	80.11(3)
P(2)–Ru(3)–Ru(2)	111.21(4)
Ru(3)–Se(1)–Ru(1)	99.27(3)
Ru(3)–Se(2)–Ru(1)	100.17(3)

Table 3
List of selected bond lengths (Å) and angles (°) for **4**

Bond lengths	
Ru(1)–Ru(4)	2.7378(14)
Ru(1)–Ru(2)	2.7705(13)
Ru(2)–Ru(3)	2.8080(15)
Ru(3)–Ru(4)	2.8156(12)
Ru(1)–Se(2)	2.6141(12)
Ru(1)–Se(1)	2.6587(13)
Ru(2)–Se(1)	2.5460(13)
Ru(2)–Se(2)	2.5650(12)
Ru(3)–Se(1)	2.5505(12)
Ru(3)–Se(2)	2.5682(13)
Ru(4)–Se(1)	2.4811(12)
Ru(4)–Se(2)	2.5815(13)
Ru(3)–P(1)	2.303(3)
Ru(4)–N(1)	2.101(7)
P(1)–C(22)	1.825(9)
N(1)–C(22)	1.341(10)
Bond angles	
Se(2)–Ru(1)–Se(1)	77.67(4)
Se(1)–Ru(2)–Se(2)	80.63(4)
Se(1)–Ru(3)–Se(2)	80.48(4)
Se(1)–Ru(4)–Se(2)	81.53(4)
Ru(4)–Ru(1)–Ru(2)	88.99(4)
Ru(1)–Ru(2)–Ru(3)	91.83(4)
Ru(2)–Ru(3)–Ru(4)	86.71(4)
Ru(1)–Ru(4)–Ru(3)	92.36(4)
Ru(4)–Se(1)–Ru(2)	100.34(4)
Ru(3)–Se(1)–Ru(1)	100.56(4)
Ru(2)–Se(2)–Ru(4)	97.21(4)
Ru(3)–Se(2)–Ru(1)	101.29(4)
P(1)–Ru(3)–Ru(2)	157.99(7)
N(1)–Ru(4)–Se(1)	151.61(18)
C(22)–P(1)–Ru(3)	115.2(3)
C(22)–N(1)–Ru(4)	115.9(6)
N(1)–C(22)–P(1)	114.6(6)

In the crystals of **4**, [$Ru_4(\mu_4\text{-}Se)_2(CO)_9\{\mu\text{-}P,N\text{-}Ph_2(2\text{-}C_5H_4N)P\}$] complexes and chloroform molecules of solvation are present. Complex **4** belongs to the family of $Ru_4(\mu_4\text{-}Se)_2$ *closo* clusters with 62 electrons and seven skeletal electron pairs. Fig. 2 shows the structure of **4** together with the atomic numbering system. Selected bond distances and angles are given in Table 3.

The cluster adopts a distorted *closo*-octahedral geometry with the four Ru atoms occupying the equatorial positions and the two Se atoms the apices. Two carbonyls bridge two adjacent edges of the Ru_4 square plane, resulting in a shortening of the Ru1–Ru2 and Ru1–Ru4 bond distances [2.770(1) and Ru1–Ru4 2.738(1) Å, respectively] [3,14,15] with respect to the other two [2.808(1) and 2.816(1) Å]. The chalcogen atoms Se1 and Se2 lie, respectively, 1.634(4) Å below and 1.671(4) Å above the Ru_4 mean plane, the eight Ru–Se bond lengths ranging from 2.481(1) to 2.659(1) Å. The structure is comparable to that of cluster [$Ru_4(\mu_4\text{-}Se)_2(CO)_9\{\mu\text{-}P,P\text{-}(Ph_2P)_2CH_2\}$] [15] in which a bisdiphenilphosphinomethane ligand (dppm) coordinates two adjacent ruthenium atoms through the phosphorous atoms. In **4** the phosphine bridges a Ru–Ru edge via the P and N atoms (Ru3–P1 and Ru4–N1 bond distances: 2.303(3) and 2.101(7) Å, respectively, see Fig. 3)

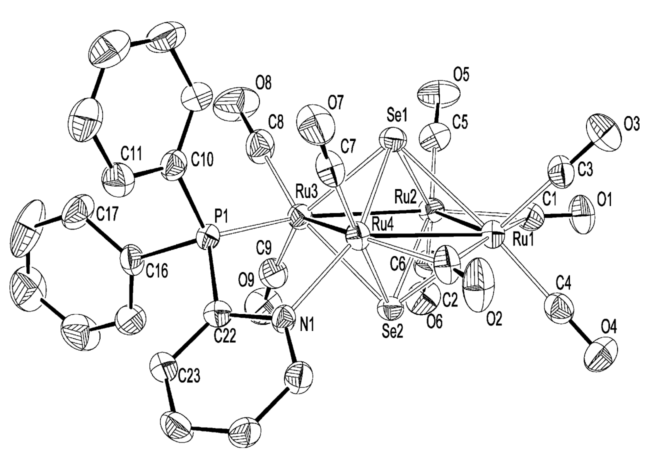


Fig. 2. View of the molecular structure of **4** together with the atomic numbering system. Thermal ellipsoids are drawn at 30% probability level.

The $Ph_2(2\text{-}C_5H_4N)P$ ligand is coordinated in such a way that the P1 atoms lies at a distance of 3.030(3) Å from the Ru4 atom, and is slightly deviated, 0.24(1) Å, from the mean plane defined by the four metal atoms; the N1–C22–P1 bond angle [114.6(6)°] is quite narrow with respect to the ideal value of 120°. The short

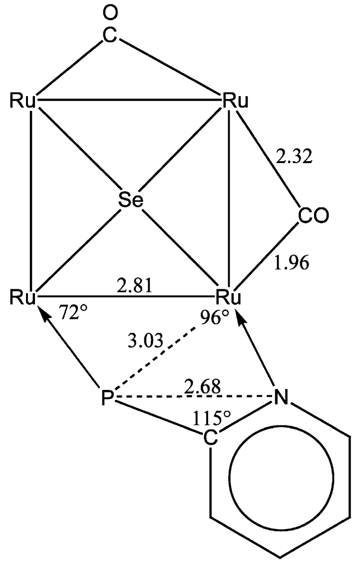


Fig. 3. Coordination mode of $Ph_2(2\text{-}C_5H_4N)P$ in $[Ru_4(\mu_4\text{-}Se)_2(CO)\{\mu\text{-}P,N\text{-}Ph_2(2\text{-}C_5H_4N)P\}]$; bond distances are given in Å.

interaction Ru···P can be viewed as a preliminary step towards the P–C bond cleavage, for the formation of a μ_2-bridged PPh_2 phosphine ligand. In this regard it is interesting to note that the Ru···P distance lies among the dozen shortest M···P interactions observed in about ninety di- or polynuclear complexes containing bridging $Ph_2(2\text{-}C_5H_4N)P$ reported in the Cambridge Data Base (2.938, 3.672, 3.265 Å min, max and mean values, respectively).

3.2. Reaction of $Ph_2(2\text{-}C_5H_4N)PSe$ with $MCl_2(PhCN)_2$ ($M = Pd$ or Pt)

Reactions between mononuclear metal complexes and phosphine selenides have already been reported in the literature, as in the case of the dppm selenide (dppmse) ligand [16]. In fact, the reaction of dppmse with metal(II) chlorides are simple coordination processes leading to complexes of the type $[M\{P,Se\text{-}Ph_2PCH_2Ph_2PSe\}_2]Cl_2$ (M = Ni, Co or Pd). From the reactions of $Ph_2(2\text{-}C_5H_4N)PSe$ with $MCl_2(PhCN)_2$ (M = Pd or Pt) it was possible to isolate and characterize the complexes $[M\{N,Se\text{-}Ph_2(2\text{-}C_5H_4N)PSe\}Cl_2]$ (**5** and **6**, respectively, for M = Pd and Pt), in which the ligand chelates the metal center via the selenium and the nitrogen atoms. Coordination through Se is suggested by the significant shift of the P=Se stretching band to low frequencies due to the M–Se interaction (569 cm^{-1} in free $Ph_2(2\text{-}C_5H_4N)PSe$, 551 cm^{-1} in the complexes). On the other hand, coordination through P is evidenced by the remarkable lowering of the $^1J(P,Se)$ coupling constant from 720 to 280 Hz in the $^{31}P\{^1H\}$ NMR spectrum, while the chemical shift is only slightly affected (δ 34.2 in complex **5**, δ 31.5 in the free ligand).

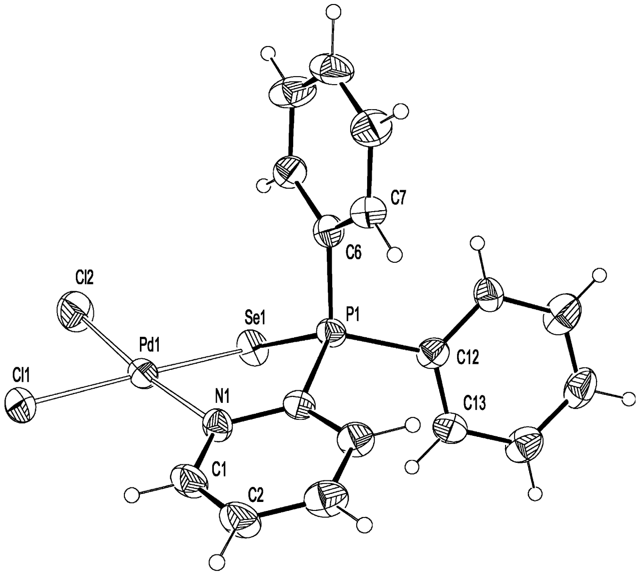


Fig. 4. View of the molecular structure of **5** together with the atomic numbering system. Thermal ellipsoids are drawn at 30% probability level.

A view of the structure of **5** is shown in Fig. 4. The most important bond distances and angles are given in Table 4.

In the mononuclear neutral palladium complex the $Ph_2(2\text{-}C_5H_4N)PSe$ acts as a chelating ligand through the Se1 and N1 atoms. The selenide phosphine ligand forms a five-membered chelating ring, with Pd1–Se1 and Pd1–N1 bond distances of 2.399(1) and 2.065(7) Å, respectively. The coordination geometry around the palladium atom is square planar [maximum deviation from the mean plane defined by Cl1, Cl2, Se1, N1, Pd1 is 0.128(3) Å for Cl1 atom]. The P–Se bond distance [2.146(2) Å] is comparable with those found in other complexes with

Table 4
List of selected bond lengths (Å) and angles (°) for **5**

Bond lengths	
Pd(1)–N(1)	2.065(7)
Pd(1)–Cl(2)	2.272(3)
Pd(1)–Cl(1)	2.348(3)
Pd(1)–Se(1)	2.3985(14)
Se(1)–P(1)	2.146(2)
N(1)–C(5)	1.361(11)
P(1)–C(5)	1.805(9)
Bond angles	
N(1)–Pd(1)–Cl(2)	174.4(2)
N(1)–Pd(1)–Cl(1)	93.4(2)
Cl(2)–Pd(1)–Cl(1)	90.94(12)
N(1)–Pd(1)–Se(1)	91.20(19)
Cl(2)–Pd(1)–Se(1)	84.76(10)
Cl(1)–Pd(1)–Se(1)	173.88(9)
P(1)–Se(1)–Pd(1)	90.48(7)
C(5)–N(1)–Pd(1)	121.4(6)
C(5)–P(1)–Se(1)	105.8(3)
N(1)–C(5)–P(1)	116.0(6)

coordinated mono- and diphosphine selenides (2.145(3) [17], 2.183(3) and 2.189(3) [18], 2.186(3) and 2.200(2) Å [19]), and significantly longer than those found in non-coordinated mono- and diphosphine selenides (2.103(3) and 2.097(4) [20], 2.108(1) [21], 2.111(3) [22], 2.085(1) and 2.101(1) Å [23]). The chelation ring exhibits an envelope conformation with the Se1 atom deviating of 0.968(1) Å from the mean plane passing through the other four atoms of the ring.

4. Supplementary material

The supplementary material for the structures includes the lists of atomic coordinates for the non-H atoms, of calculated coordinates for the hydrogen atoms, of anisotropic thermal parameters and complete lists of bond lengths and angles. The details of the crystal structure investigations have been deposited with the Cambridge Crystallographic Data Center CCDC Nos. 168273 (**3**·CH_2Cl_2), 168274 (**4**·0.5$CHCl_3$) and 168275 (**5**). Copies of the data can be obtained free of charge on application to The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44-1223-336-033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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